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Trace-element and multi-isotope geochemistry of Late-Archean black shales in the Carajás iron-ore district, Brazil

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ABSTRACT

The 250–300-m-thick Carajás Formation in the Carajás mineral province, northern Brazil, consists of banded iron formation (including giant high-grade iron-ore deposits) and minor black shale, overlying a thick pile (2–3 km) of about 2.75-Ga-old metabasalt. Carbonaceous shale with pyrite- and locally pyrrhotite-rich patches from drillcore of the Serra Sul exploration project has up to 29 ppm Mo; iron-speciation analysis indicates essentially ferruginous and for some samples likely euxinic depositional conditions. Positive δ^{34}S-isotope ratios of TRIS are between +0.3 to +10.7‰, with heavy data restricted to pyrrhotite-free samples. The data suggest microbial sulfate reduction under, at least partially, sulfate-limiting conditions with later overprint by migrating solutions. The black shale is affected by pronounced low-temperature potassium metasomatism ($K_2O/Na_2O > 100$; up to 10 wt.% K_2O as adularia) related to diagenetic processes at <100 °C, and low-grade metamorphic overprint. We studied a 20-cm-black-shale drillcore interval from the middle part of the Serra Sul BIF sequence in detail. Five samples with the most euxinic signature give a Re–Os regression of 2710 ± 38 Ma (2σ) with an initial ratio of −0.37 ± 0.40 (MSWD = 3.3), whereas the full data set (n = 11), including black-shale samples from the top and bottom of the BIF sequence, gives a regression of 2661 ± 110 Ma (MSWD = 121). Molybdenum-isotope patterns suggest mixing between a clastic end member, with about 0.2‰ $\delta^{98/95}$Mo for continental input (T_{DM} of 2.8–3.1 Ga according to Nd-isotope data), and 0.9‰ $\delta^{98/95}$Mo for a hydrogenous component. Black-shale samples from the bottom of the BIF sequence have heavy Mo-isotope composition of up to 1.8‰ $\delta^{98/95}$Mo. The significant Mo-isotope fractionation is either the result of an early and transient "whiff of oxygen" at 2.7 Ga, or the result of hydrothermal fluid overprint.

1. Introduction

The Late-Archean banded iron formation (BIF) of the Carajás mineral province in the eastern part of the Amazon craton hosts one of the largest iron-ore resources on Earth. The still undeveloped giant Serra Sul iron-ore deposit comprises four orebodies (Coelho, 1986), one of which is Serra Sul D, with 9-Gt ore at a grade of 67% Fe. Drilling of the Serra Sul D orebody intercepted several small units of sulfide-containing black shale on top, in between and at the bottom of the 250–300-m-thick BIF. We sampled two drillcores at a drilling depth within 200 and 320 m, i.e. below the level of weathering and high-grade iron-ore formation. These black-shale units have an age of around 2.7 Ga (this study) and record valuable information on the seawater redox conditions at that time.

Here we describe the Serra Sul black shale and provide geochemical data (bulk-rock chemistry, Mo and S isotopes, as well as Re–Os and Sm–Nd isotopes). The black-shale sedimentation took place at a time when transient geochemical signals first indicate incipient oxygenation of the atmosphere and oceans (Kaufman et al., 2007; Wille et al., 2007; Frei et al., 2009; Reinhard et al., 2009; Voegelin et al., 2010). The data from redox-sensitive trace elements in sulfide-bearing black shale complement information from coeval iron-oxide BIF, which formed under sulfide-free conditions (Klein and Ladeira, 2002; Fabre et al., 2011).

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2. Geological setting

The BIF of the Carajás mineral province in northern Brazil is part of the Late-Archean Grão Pará Group of the Itacaiúnas Supergroup (DOCEGEO, 1988), and encompasses a lower unit of metabasalt (3–4 km; the Parauapebas Formation), a middle unit of BIF and minor clastic rocks (100–300 m; the Carajás Formation, Beisiegel et al., 1973), and an upper unit of meta-basalt and clastic rocks (400–500 m; the Igarapé Cigarra Formation). The Grão Pará Group rests on a gneiss–granite metamorphic basement with ages of >2.8 Ga, has low or very low metamorphic grade, and is unconformably overlain by a thick clastic sequence, the Águas Claras Formation, which hosts important manganese deposits. The age of the BIF sequence is about 2.75 ± 0.02 Ga, constrained by U–Pb zircon dating of ill-defined "probable tuff" from weathered BIF rock at Serra Norte (Olszewski et al., 1989; Macambira et al., 1996; Trendall et al., 1998). The age of the overlying Águas Claras Formation could be <2.4 Ga in the light of recent multiple S-isotope patterns from diagenetic pyrite in these rocks, which are not affected by mass-independent S-isotope fractionation (Fabre et al., 2011).

The volcanic rocks of the Grão Pará Group mainly comprise basalt and basaltic andesite with the mineral assemblage of actinolite–chlorite–epidote–quartz–calcite (Teixeira and Eggler, 1994), which were interpreted as low-grade regional metamorphism, but could also derive from subseafloor hydrothermal alteration during volcanism (e.g., Zucchetti, 2007). The rocks have low Zr, Nb, and Ti contents, and have calc-alkaline affinity, suggesting an island-arc environment (Teixeira and Eggler, 1994). However, other authors provided geochemical evidence that the Grão Pará Group originated from rifting of continental crust (Olszewski et al., 1989), or attenuated continental crust in a back-arc setting (Zucchetti, 2007).

The most conspicuous structural feature of the region is a WNW-trending fold system, about 200-km long and 30–40-km wide, intersected by the Carajás strike-slip system (e.g., Pinheiro and Holdsworth, 1997), which separates Serra Norte and Serra Sul (Fig. 1). The Serra dos Carajás granite, also known as the Central Carajás granite, intruded the Carajás strike-slip system at 1.9 Ga (Machado et al., 1991). The BIF of the Carajás Formation is exposed in the northern limb (Serra Norte) and southern limb (Serra Sul); the latter is thus a partially disrupted *s*-shaped synform–antiform pair (Rosière et al., 2006). The exposures are along elongated flat ridges with little vegetation, standing out some 100–200 m above the jungle-covered lowlands. These plateaux represent Cretaceous–Cenozoic ferricrete erosion surfaces with a prolonged history of deep lateritic weathering and an exceptionally low rate of surface erosion of less than 1 m/Ma over the last few millions of years (Shuster et al., 2012), which allowed extreme residual enrichment to spectacular high-grade iron-ore deposits.

The ferricrete or ferruginous duricrust (termed "canga" in Brazil) is up to 20 m in thickness (e.g., Tolbert et al., 1971) and consists of detrital

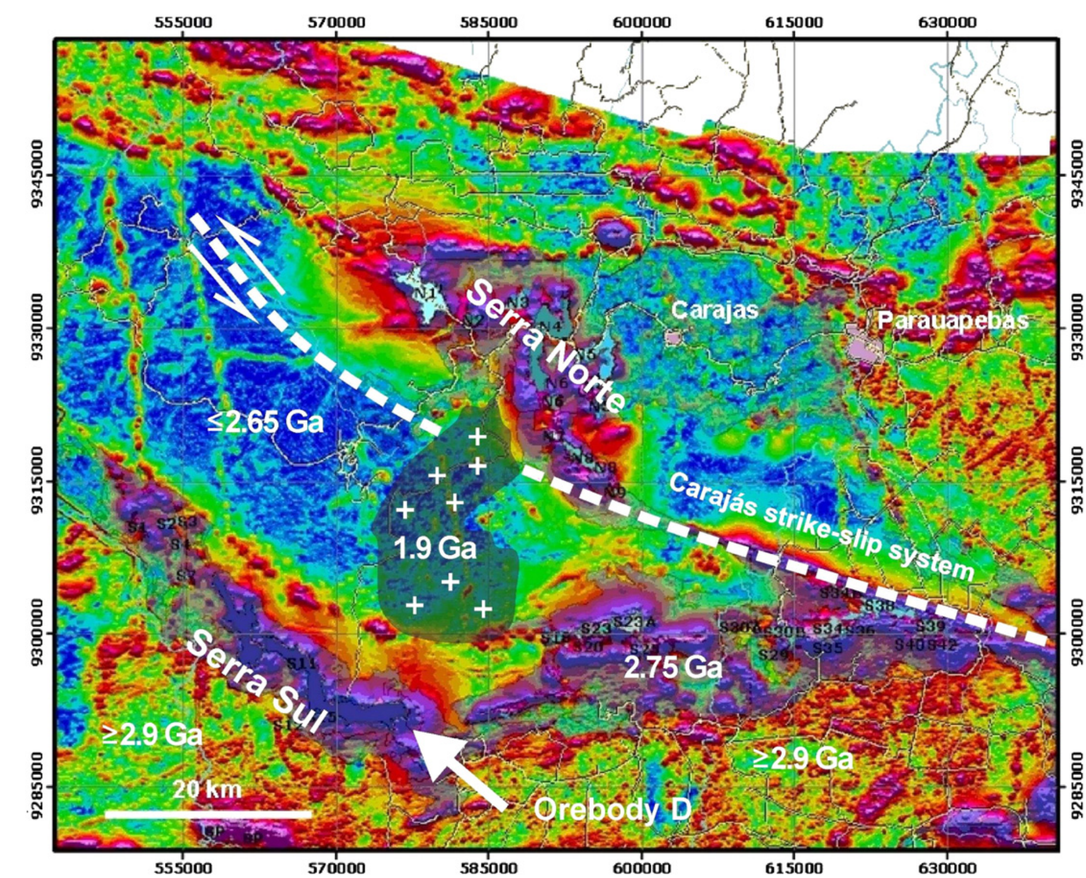

Fig. 1. Aeromagnetic map of the eastern part of the Carajás mineral province. The strongly magnetic rocks of the ~2.7-Ga banded iron formation (Carajás Formation) in violet–blue color define a NW-trending open syncline, with the major high-grade iron-ore deposits of Serra Norte in the north and Serra Sul in the south. The central part of the map is formed by the overlying Águas Claras Formation (mostly clastic rocks), and the large intrusion of the anorogenic 1.9-Ga Serra dos Carajás granite. The 2.75-Ga metabasalt of the Parauapebas Formation immediately underlies the 250–300-m-thick banded iron formation, resting on ≥2.9-Ga metamorphic gneiss–granite basement, which is exposed to the north and south of the synclinal structure. The outline of the Serra dos Carajás granite is added here, as it does not show up in the aeormagnetic map. We studied drillcore from Orebody D (9 Gt @ 67% Fe) of the Serra Sul project, by VALE, which is currently under development for mining.